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The magnetic properties of praseodymium, neodymium, gadolinium, holmium, erbium, and lutetium phthalocyanines are described according to magnetic susceptibility measurements measured in the 80-300 K or 4.2-300K range. Sigma and pi interactions between the pyrrolic nitrogen ligand and the f-orbitals of praseodymium, neodymium, holmium, and erbium were obtained using the angular overlap model (AOM). The calculations included the complete ground-state manifold of the respective lanthanide ions. The position of the pyrrolic nitrogen ligand in the metallic two dimensional spectrochemical series is presented. The results show that the pyrrolic nitrogen is a weak sigma donor and a moderate pi donor.

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Aplicacion Del Medelo De Traslape Angular A

Ftalocinaninas De Lantanidos

(Application of the Angular Overlap Model to
Lanthanide Phthalocyanines)

by

Juan Padilla and William E. Hatfield

The Department of Chemistry, The University of North
Carolina at Chapel Hill, North Carolina, 27599, U.S.A.

APLICACION DEL MODELO DE TRASLAPE ANGULAR

A FTALOCINANINAS DE LANTANIDOS

Juan Padilla,* (1) y William E. Hatfield (2).

(1) Departamento de Quimica, Universidad Autónoma Metropolitana, Iztapalapa. A. P. 55-534, México, D.F. 09340
(2) Department of Chemistry, University of North Carolina at Chapel Hill, NC 27599-3290.

Introduccion.

El modelo de traslape angular (MTA) [1-3] permite obtener en forma cuantitativa la magnitud relativa y el signo de las interacciones σ y π de ligantes con iones metálicos. Esto trae a la teoria del campo ligante el concepto de grupos funcionales. En este trabajo se usó el enfoque del MTA desarrollado por Gerloch et. al.[2]

Siendo el MTA un modelo paramétrico, para poder calcular los valores de los parámetros se requirere ajustarlos a los datos experimentales. Un metodo experimental de obtener las interacciónes σ y π de los ligantes con metales es la espectroscopia de absorción (UV-Vis-IR). Las interacciónes σ y π se pueden obtener a partir de las energias de transición e interpretarlas usando el MTA. Sin embargo, en el caso de las ftalocianinas de los lantánidos, tales estudios se dificulian por dos razones. Primero, proque las transiciones f-f son prohibidas y por de tanto de intensidad débil. Segundo, porque las bandas $\pi \rightarrow \pi^*$ del macrociclo de la ftalocianina son intensas y obscurecen las bandas f-f mas débiles, las cuales se requireren para el análisis. Este obstáculo se puede vencer con ayuda de mediciones de susceptibilidad magnética.

En este trabajo, se determinaron los parámetros del MTA a partir de los datos de susceptibilidad magnética (80-300 K) para los compuestos de ftalocianinas de praseodimio, neodimio, holmio y erbio. También se determinó la posición de los comeuestos en la serie espectroquimica metálica bidimensional.

Resultados y Discusión.

Las ftalocianinas de los lantánidos H(Pc)Ln(PC) (Pc – dianion ftalocianinato, Ln = Pr, Nd, Gd, Ho y Er) se prepararon por una modificación de la sintesis descrita en las literatura [4]. Los productos se caracterizaron con ayuda de los espectros de IR, UV-Vis y RPE.

Usando el algoritmo SIMPLEX [5], se ajustaron los datos de susceptibilidad magnética a la ecuación de Curie-Weiss resultando los parámetros de la Tabla 1.

Table 1. Parametros de Curie-Weiss para ftalocianinas lantanoides

Compuesto	C (uem K mol^{-1})	θ(K)
H(Pc)Pr(Pc)	1.90	-110
H(Pc)Nd(Pc)	1.17	-61
H(Pc)Gd(Pc)	6.61	6
H(Pc)Ho(Pc)	13.0	0
H(Pc)Er(Pc)	8.83	-4

Las constantes de Weiss, θ, para las ftalocianinas de praseodimio y neodimio y neodimio son más grandes que las observadas en las otras ftalocianinas. Hay dos explicaciones posibles para racionalizar las diferencias; ya sea que los iones

lantánido muestran fenómenos cooperativos, o bien el
paramagnetismo independiente de la temperature (PIT) es
considerable. El signo negativo para Θ implica acoplamiento de
intercambio antiferromagnético; sin embargo, en tales casos se ha
observado que la temperatura de Neel, T_N, es aproximadamente
igual al negativo de la constante de Weiss ($\Theta = -T_N$) [6]. Eso
quiere decir que el ordenamiento magnético deberia observarse
alrededor de 110 y 61 K para las ftalocianinas de praseodimio y
neodimio, respectivamente. Sin embargo, las mediciones de
susceptibilidad magnética hasta 4.2 K no dan alguna indicación de
acoplamiento de intercambio, y eso descarta la primera
posibilidad.

Por otra parte, el PIT proviene de la mezcla en el estado
fundamental de estados excitados energéticamente bajos que no
están poblados térmicamente [7]. De los cinco iónes lantánido
considerados en este estudio, praseodimio y neodimio son
precisamente los que tienen el primer estado excitado de energia
más baja, y de qui que sean los únicos que muestram PIT
apreciable.

Para hacer los cálculos usando el MTA, se diagonalizó el
multiplete completo del estado fundmental usando una base del
ion-libre bajo un potencial de campo ligante, y el cálculo
posterior de las susceptibilidades magnéticas se hizo de acuerdo
a la teoria de perturbaciones usando la ecuación de Van Vleck.
Es importante recordar que a pesar de que los efectos del campo
ligante en lantánidos representan solo una perturbación pequeña
desde el punto de vista de la espectro copia electrónica, ellos

son la esencia de sus propiedades magneticas. Los mejores

ajustes de los parámetros se enlistan en la Tabla 2.

Tabla 2. Parámetros del MTA en números de onda

Parametro	H(Pc)Pr(Pc)	H(Pc)Nd(Pc)	H(Pc)Ho(Pc)	H(Pc)Er(PC)
e_α	117	126	153	155
$e_{\pi y}$	33	41	49	72
$e_{\pi \sigma}$	0.28	0.33	0.32	0.46
% Error	2.8	2.0	0.8	3.2

No fué posible obtener buenos ajustes cuando el parámetro

mixto $e_{\pi\sigma}$ se conservó constante e igual a cero. Este no es un

resultado inesperado ya que generalmente se observa en compuestos

quelato [8]. Dicho parámetro representa el grado de mezcla entre

los orbitales σ y π en los átomos de nitrógeno, puesto que en las

ftalocianinas de los lantánidos el orbital σ del nitrógeno no

está orientado en la posición que favorece el máximo traslape

orbital. Esto se conoce como la contribución de la valencia mal

dirigida [9]. La contribución se tomó en cuenta añadiendo los

términos extra Y_2^1, Y_4^1 y Y_6^1 en la expansión de los armónicos

esféricos. Los mismos parámetros mejor ajustados se obtuvieron

independientemente usando el algoritmo de optimización GRADX

[10].

Los resultados de este trabajo muestran la validéz del MTA

aplicado a ftalocianinas de lantánidos. Los parámetros del MTA

reflejan la naturaleza del enlace metal-ligante en el complejo.

El signo positivo de e_σ y e_π y indican las propiedades donadoras del enlace σ y π, respectivamenta del átomo de nitrógeno, y la magnitud indica la fortaleza del enlace Ln-N [2]. Los valores de e_σ y $e_{\pi y}$ son pequeños comparados con los que usualmente se obtiene para compuestos de metales de transición. Esto es un reflejo del efecto de apantallamiento que occure en la serie de los lantánidos, asi como de la covalencia débil del enlace Ln-N las propiedades donadoras del átomo de nitrógeno pirrólico se pueden explicar considerando que en el anillo pirrólico la deslocalización en el grupo imino es pequeña, y el sistema no se altera mucho debido a la donación π.

A partir de los ajustes se encontró que $e_{\pi y}$ es mayor al valor ideal 0.25 e_σ que se basa en la relación de integrales de traslape σ y π de funciones de ondo s y p puras en los átomos de nitrógeno, por lo que se puede concluir que los atomos de nitrógeno pirrólicos se compartan como donadores σ débiles y donadores π moderados.

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APLICATION OF THE ANGULAR OVERLAP MODEL TO LANTHANIDE PHTHALOCYANINES.

Juan Padilla* (1) and William E. Hatfield (2).

(1) Departamento de Quimica, Universidad Autonoma Metropolitana Iztapalapa, A.P. 55-534, Mexico, D.F. 09340.
(2) Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27599-3290.

Abstract.

The magnetic properties of praseodymium, neodymium, gadolinium, holmium, erbium, and lutetium phthalocyanines are described according to magnetic susceptibility measurements measured in the 80-300 K or 4.2-300 K range. Sigma and pi interactions between the pyrrolic nitrogen ligand and the f-orbitals of praseodymium, neodymium, holmium, and erbium were obtained using the angular overlap model (AOM). The calculations included the complete ground-state manifold of the respective lanthanide ions. The position of the pyrrolic nitrogen ligand in the metallic two-dimensional spectrochemical series is presented. The results show that the pyrrolic nitrogen is a weak sigma donor and a moderate pi donor.

Introduction.

The angular overlap model (AOM) [1,2] allows to obtain quantitatively the relative magnitude and the sign of the sigma and pi interactions of ligands with metal ions. This brings to ligand-field theory the concept of functional groups.

Being the AOM a parametric model, in order to calculate the parameters it is required to adjust them to the experimental values. Absorption spectroscopy (UV-VIS-IR) provides an experimental tool to obtain the sigma and pi interactions between ligands and metals. They can be calculated from the transition energies, and the interpretation accomplished using the AOM. However, in the case of lanthanide phthalocyanines, such studies are difficult for two reasons. First, the f-f transitions are parity forbidden and therefore of weak intensity. Secondly, the pi ---> pi* bands of the macrocycle phthalocyanine are intense, and obscure the weaker f-f bands which are required for the analysis. This obstacle may be overcome with help of magnetic susceptibility measurements.

In this work, magnetic susceptibility measurements (80-300 K or 4.2-300 K) were used to determine the AOM parameters of praseodymium, neodymium, holmium, and erbium phthalocyanines. Also, the position of the compounds in the two-dimensional spectrochemical series was determined.

Results and Discussion.

The lanthanide phthalocyanines H(Pc)Ln(Pc) [Pc = dianion phthalo-
cyaninato, Ln = Pr, Nd, Gd, Ho, Er, and Lu] were prepared by a
modification of the synthesis described in the literature
[3]. The products were characterized with help of the IR, UV-VIS,
and EPR spectra.
        Using the algorithm SIMPLEX [4], the magnetic susceptibility
data were fitted to a Curie-Weiss equation resulting in the
parameters shown in Table 1.

Table 1. Curie-Weiss parameters for lanthanide phthalocyanines.

Compound	C (emu K mole^{-1})	θ (K)
H(Pc)Pr(Pc)	1.90	- 110
H(Pc)Nd(Pc)	1.17	- 61
H(Pc)Gd(Pc)	6.61	6
H(Pc)Ho(Pc)	13.0	0
H(Pc)Er(Pc)	8.83	- 4

        The Weiss constants, θ, for praseodymium and neodymium
phthalocyanines are larger than those observed in the other
phthalocyanines. There are two possible explanations to rational-
ize the differences; either the lanthanide ions show cooperative
phenomena, or the temperature independent paramagnetism (TIP) is
considerable. The negative sign for θ implies antiferromagnetic
exchange coupling; however, in such cases it has been observed
that the Neel temperature TN is approximately equal to the
negative of the Weiss constant (θ = - TN) [5]. That means the
magnetic ordering should be observed at about 110 and 61 K for
praseodymium and neodymium phthalocyanines, respectively. Magne-
tic susceptibility measurements collected down to 4.2 K however
show no indication of exchange coupling, ruling out the former
possibility.
        On the other side, the TIP arises from the mixture into the
ground state of thermally non populated, yet low lying excited
states [6]. Of the five lanthanide ions considered in this study,
praseodymium and neodymium are precisely the ones with the lowest
lying excited states, and therefore the only ones that should
show appreciable temperature independent paramagnetism.
        Calculations using the AOM were carried out as follows. The
calculations involve the diagonalization of the complete ground-
state manifold of the free-ion basis under the ligand-field
potential, and a subsequent computation of magnetic susceptibili-
ties by perturbation theory within the Van Vleck equation. It is
important to remember that even ligand-field effects in lantha-
nide compounds represent only small perturbations from the point
of view of electronic spectroscopy, they are the essence of their
magnetic behavior.
        The best-fit parameters are listed in Table 2.

Table 2. AOM best-fit parameters in wavenumbers.

Parameter	H(Pc)Pr(Pc)	H(Pc)Nd(Pc)	H(Pc)Ho(Pc)	H(Pc)Er(Pc)
e_σ	117	126	153	155
$e_{\pi y}$	33	41	49	72
$e_{\pi \sigma}$	10	10	12	2
$e_{\pi y}/e_\sigma$	0.28	0.33	0.32	0.46
% Error	2.8	2.0	0.8	3.2

It was not possible to get good fittings when the cross-term parameter, $e_{\pi\sigma}$, was set equal to zero, and kept constant during the fittings. This is not an unexpected result, since it is generally found in chelate compounds [7]. The cross-term parameter represents the degree of admixture between the sigma- and pi-orbitals in the nitrogen atoms, since in the lanthanide phthalocyanines the nitrogen sigma-orbital is not oriented in the position that favors the maximum orbital overlap. This is the so-called misdirected valency contribution to the ligand-field potential [8]. The cross-term contribution was taken into account by adding the extra terms Y21, Y41, and Y61 in the ligand-field spherical harmonics expansion. The same best-fit parameters were obtained independently with the optimization algorithm GRADX [9].

The results of this work show the validity of the AOM as applied to lanthanide phthalocyanines. The AOM parameters reflect the nature of the metal-ligand bond in the complex. The positive signs of e_σ and $e_{\pi y}$ indicate the sigma- and pi-donor properties of the nitrogen atom, respectively, and the magnitude indicates the strength of the Ln-N bond [2]. The values of e and $e_{\pi y}$ are small compared to the values usually obtained for transition metal ions. This is a reflection of the screening effect that occurs in the lanthanide series, and of the weak covalency of the Ln-N bond. The donor properties of the pyrrolic nitrogen atom may be explained considering the small delocalization in the imine group, and little disruption is caused by pi-donation.

From the fittings, it was found $e_{\pi y}$ to be greater than the ideal value of 0.25 e_σ based on the ratio of sigma- and pi-overlap integrals of pure s- and p-wavefunctions on the nitrogen atoms. Therefore, it can be concluded that the pyrrolic nitrogen atoms behave as weak sigma-donors, and moderate pi-donors.

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